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Molecular Engineering of Liquid Crystal Polymers by Living Polymerization. 20.
Synthesis and Characterization of Binary Copolymers of 11-[4-Cyano-4'-biphenyl)
oxy]undecanyl Vinyl Ether with n-Butyl Vinyl Ether and of 2-[4-Cyano-4'-
biphenyl)oxy]ethyl Vinyl Ether with n-Butyl Vinyl Ether

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INTRODUCTION

Copolymerization represents the simplest synthetic technique which can be used to tailor make phase transitions of both main chain^{1a} and side chain^{1b} liquid crystalline polymers. Indeed, copolymerization was frequently employed to manipulate the phase transitions of side chain liquid crystalline polymers.¹⁻⁵ However, most of the results reported in the literature can be considered only in a qualitative way, since there are only very few cases in which information about both copolymer composition and molecular weight are available.^{1b-6}

A general classification of side chain liquid crystalline copolymers⁵ was recently discussed in a review article.^{1b} There are two main classes of side chain liquid crystalline copolymers. The first one refers to copolymers containing pairs of structural units with and without mesogenic units. The second class refers to copolymers based on pairs of structural units containing mesogenic units in each structural unit.

There has been much interest in copolymers derived from structural units containing mesogenic units and non-mesogenic units since the mesophase of the resulted copolymers is preserved even for a very low content of mesogenic groups.¹⁻¹⁵ Therefore, one of the important advantages of the method of copolymerization of mesogenic and non-mesogenic monomers consists in the possibility of varying the temperature range of the mesophase. The general trend is that the glass transition temperature changes gradually between the glass transition temperatures (T_g) of the respective homopolymers as the copolymer composition is changed. In all cases a non-mesogenic monomer is chosen so as to lower the T_g of a copolymer relative to the T_g of the parent liquid crystalline homopolymer. This is achieved because copolymerization of a mesogenic monomer with a non-mesogenic monomer dilutes the concentration of mesogenic units of the polymer. Subsequently, the copolymer loses its mesomorphic behavior below a minimum concentration of the mesogenic groups. This concentration is determined by the the nature of both monomers. Consequently, both the glass transition and the isotropization temperatures are affected by the content of the non-mesogenic comonomer. Also, apart from their basic liquid crystalline behavior, the structural and miscibility properties of these copolymers are strongly modified.¹⁵

However, there are few systematic investigations on the phase behavior of copolymers containing mesogenic and non-mesogenic structural units^{11,12}. Although the compositions of these copolymers were reported, molecular weight information was available only in few cases.^{11,12} Liquid crystalline copolysiloxanes are prepared by hydrosilation reactions. They are considered to be statistical copolymers with a random distribution of their structural units.^{1b,11,16} Copolymers synthesized by chain copolymerization reactions exhibit a heterogeneous composition unless they are prepared at low conversions.^{1b} At the same time until a while ago, there was no single example in the literature in which the molecular weights of statistical side chain liquid crystalline copolymers prepared by chain copolymerizations were reported.^{1b,3,5,17-19} Since

mesomorphic transitions are molecular weight dependent,^{1b,11,20-28} the synthesis of copolymers with both well defined composition and molecular weight are required in order to understand their phase behavior. The ideal solution to the synthesis of copolymers by chain reactions would be to select monomer pairs which follow an azeotropic copolymerization mechanism and can be prepared by a living polymerization reaction. Such systems require $r_1=r_2=1$ and are encountered mainly for comonomer pairs with identical polymerizable groups.

Vinyl ethers containing a mesogenic group are presently one of the most suitable monomers for these investigations because they can be polymerized by a living mechanism.²³⁻²⁸ Previous publications from our laboratory reported the first examples of quantitative experiments on side chain liquid crystalline copolymers prepared from monomer pairs containing identical mesogenic groups and polymerizable groups, but different spacer lengths, with constant degrees of polymerization, narrow molecular weight distributions and variable composition.^{28b,c,29}

This paper will describe the synthesis and characterization of poly{11-[4-cyano-4'-biphenyl]oxy]undecanyl vinyl ether-co-n-butyl vinyl ether}X/Y {poly[(6-11)-co-(BVE)]X/Y and poly{2-[4-cyano-4'-biphenyl]oxy]ethyl vinyl ether-co-n-butyl vinyl ether}X/Y {poly[(6-2)-co-(BVE)]X/Y. Therefore, the investigation of these two pairs of copolymers will provide a quantitative elucidation of the phase behavior of copolymers derived from pairs of mesogenic and non-mesogenic monomers.

EXPERIMENTAL

Materials

All materials were commercially available and were used as received or purified as described previously.^{27a,b} n-Butyl vinyl ether (98%, Aldrich) was first washed with diluted aqueous KOH, then with water, dried first over anhydrous magnesium sulfate, then over sodium, and finally freshly distilled under vacuum. Methyl sulfide (anhydrous, 99%,

Aldrich) was refluxed over 9-borabicyclo[3.3.1]nonane (9-BBN, crystalline, 98%, Aldrich) and then distilled under argon. Dichloromethane (99.6%, Aldrich) used as a polymerization solvent was first washed with concentrated sulfuric acid, then with water, dried over anhydrous magnesium sulfate, refluxed over calcium hydride and freshly distilled under argon before each use. Trifluoromethane sulfonic acid (triflic acid, 98%, Aldrich) was distilled under argon.

Techniques

^1H -NMR (200 MHz) spectra were recorded on a Varian XL-200 spectrometer. TMS was used as internal standard. A Perkin Elmer DSC-4 differential scanning calorimeter equipped with a TADS 3600 data station was used to determine the thermal transitions which were reported as the maxima and minima of their endothermic and exothermic peaks respectively. In all cases, heating and cooling rates were $20^\circ\text{C}/\text{min}$ unless otherwise specified. Glass transition temperatures (T_g) were read at the middle of the change in the heat capacity. For certain polymer samples, the first heating scans sometimes differ from the second and subsequent heating scans. At the proper place, this difference will be mentioned. However, the second and subsequent heating scans are identical. The first heating scans can be obtained again after annealing above T_g but below the melting temperature of the polymer sample. This is because the crystallization process is kinetically controlled while the formation of the mesophase is thermodynamically controlled. Therefore, crystallization is a slow process while the formation of the mesophase is a fast process. A Carl-Zeiss optical polarized microscope (magnification: 100x) equipped with a Mettler FP 82 hot stage and a Mettler FP 800 central processor was used to observe the thermal transitions and to analyze the anisotropic textures.^{30,31} Molecular weights were determined by gel permeation chromatography (GPC) with a Perkin Elmer series 10 LC instrument equipped with LC-100 column oven, LC-600 autosampler and a Nelson analytical 900 series integrator data station. The measurements were made at 40°C using the UV detector. A set of Perkin Elmer PL gel columns of 10^4 and 500 \AA with CHCl_3 as

solvent (1ml/min) and a calibration plot constructed with polystyrene standards was used to determine the molecular weights. Therefore, all molecular weights discussed in this paper are relative to polystyrene. High pressure liquid chromatography (HPLC) experiments were performed with the same instrument.

Synthesis of Monomers

11-[(4-Cyano-4'-biphenyl)oxy]undecanyl vinyl ether (6-11)^{27a} and 2-[(4-cyano-4'-biphenyl)oxy]ethyl vinyl ether (6-2)^{27b} were synthesized and purified as described in previous publications. Their purity was higher than 99% (HPLC). Their detailed characterization was described in the previous publications.

Cationic Polymerizations and Copolymerizations

Polymerizations were carried out in glass flasks equipped with teflon stopcocks and rubber septa under argon atmosphere at 0°C for 1 hr. All glassware was dried overnight at 130°C. The monomer was further dried under vacuum overnight in the polymerization flask. Then the flask was filled with argon, cooled to 0°C and the methylene chloride, dimethyl sulfide and triflic acid were added via a syringe. The monomer concentration was about 10 wt% of the solvent volume and the dimethyl sulfide concentration was 10 times larger than that of the initiator. The polymer molecular weight was controlled by the monomer/initiator ($[M]_0/[I]_0$) ratio. After quenching the polymerization with ammoniacal methanol, the reaction mixture was precipitated into methanol. When necessary, the polymers were reprecipitated until their GPC and HPLC traces showed complete absence of unreacted monomers. Tables I and II summarize the polymerization results. Although polymer yields are lower than expected due to losses during the purification process, conversions determined by GPC and NMR analyses before polymer purification were almost quantitative in all cases.

RESULTS AND DISCUSSION

The synthesis, characterization and living cationic polymerization of 11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether (6-11) and 2-[(4-cyano-4'-biphenyl)oxy]ethyl vinyl ether (6-2) were described in the previous papers.^{27a,b} Our preferred initiating system is $\text{CF}_3\text{SO}_3\text{H}/\text{S}(\text{CH}_3)_2$ ³² since it can be used to perform living cationic polymerizations in CH_2Cl_2 at 0°C. In addition, we have shown that this system can be used to initiate the living cationic polymerization, cyclopolymerization and copolymerization of monomers containing a variety of functional groups.^{28,33} Scheme I outlines the copolymerization of mesogenic vinyl ethers with the non-mesogenic vinyl ether. Although the yields reported in Tables I and II are lower than quantitative due to polymer losses during the purification process, all copolymerizations lead to almost quantitative conversions (determined by NMR and GPC). In all cases, the copolymer composition corresponds with the comonomer feed composition which was determined by ¹H-NMR spectroscopy experiments. The GPC traces of all copolymers show a monomodal molecular weight distribution characterized by a polydispersity lower than 1.15 (Tables I and II). Attempts were made to synthesize all copolymers with degrees of polymerization of about 20.

According to the nature of the highest temperature mesophase exhibited by the homopolymers generated from the mesogenic monomers used in the synthesis of these copolymers, we can classify these experiments into two classes. Poly[(6-11)-co-(BVE)]X/Y copolymers are based on a mesogenic monomer whose parent homopolymer exhibits an enantiotropic S_A phase as the highest temperature mesophase. Poly[(6-2)-co-(BVE)]X/Y copolymers are based on a mesogenic monomer whose parent homopolymer exhibits a glassy phase as the highest temperature phase when it is determined from the second heating scan. The second comonomer from both copolymers leads to a glassy polymer poly(BVE).

Poly[(6-11)-co-(BVE)]X/Y

The synthesis and characterization of poly[(6-11)-co-(BVE)]X/Y copolymers are summarized in Table I. The first and the second heating, and the first cooling DSC scans of homopolymer and copolymers are presented in Figure 1a-c. As determined from the first DSC heating scans, poly(6-11) with a degree of polymerization of 19 exhibits an enantiotropic S_A mesophase and a crystalline melting. When the phase behavior of the same polymer is determined from the second and subsequent heating scan, it exhibits enantiotropic S_A and S_X (unidentified smectic phase) mesophases.^{27a} On the optical polarized microscope the S_A phase exhibits a focal conic texture. Representative textures of this mesophase were published previously.^{27a} Let us first discuss the phase behavior of poly[(6-11)-co-(BVE)]X/Y as obtained from the first DSC heating scans. The first DSC heating scans of these copolymers are presented in Figure 1a. Upon copolymerization, the temperature associated with the S_A -isotropic phase transition decreases continuously. Poly[(6-11)-co-(BVE)]1/9 does not exhibit any mesophase. Therefore, the structural unit derived from the monomers 6-11 and BVE are isomorphic³⁴ within the S_A phase over a very broad range of compositions. Copolymers with X/Y=10/0 to 7/3 exhibit both the S_A and the crystalline phases. The temperatures associated with k- S_A transition (Figure 1a) show almost constant values regardless of copolymer composition. Therefore, within the crystalline phase the two structural units are isomorphic over a very narrow range of compositions.

In the second DSC heating scan, the crystalline phase does not appear, while the S_A mesophase follows the same trend as the one observed in the first DSC heating scans (Figure 1a,b). The cooling DSC scans (Figure 1c) are following a similar trend as that observed in the second DSC heating scans (Figure 1b). The S_A phase of poly[(6-11)-co-(BVE)]X/Y with X/Y from 2/8 to 9/1 exhibits a similar focal conic texture as that displayed by poly(6-11).^{27a}

The phase transition temperatures collected from the first heating scans are plotted in Figure 2a, and those from the second heating and the first cooling scans in Figure 2b.

These plots show continuous and linear dependences of the S_A -i and i- S_A phase transition temperatures on copolymer composition for poly[(6-11)-co-(BVE)]X/Y with X/Y=2/8 to 10/0. Figure 3 plots the dependence of the enthalpy change associated with the S_A phase transition as a function of copolymer composition. This plot shows very clearly the continuous character of the dependence of enthalpy changes versus copolymer composition over a broad range of copolymer compositions. An attempt to extrapolate the linear dependence of the enthalpy change associated with the S_A -i and i- S_A phase transition to poly[(6-11)-co-(BVE)]1/9 leads to a value of $\Delta H=0$ which demonstrates that poly[(6-11)-co-(BVE)]1/9 does not exhibit a S_A mesophase. Therefore, poly[(6-11)-co-(BVE)]X/Y copolymers preserve the S_A mesophase even at as low as 20 mole% of mesogenic units, however, it disappears at lower contents of mesogenic monomer units. Figure 4 presents the dependence of the peak width of the S_A -isotropic transition temperature versus copolymer composition. The peak width increases with increasing the non-mesogenic unit content as can be qualitatively observed from the DSC traces from Figure 1. The broadening of the peak width may be due to a higher interfacial mixing between the higher content of polymer backbone without mesogenic groups and the mesogenic side groups in the S_A phase.^{11,12}

In conclusion, the results of the investigation of the poly[(6-11)-co-(BVE)]X/Y suggest a synthetic technique that can be used to molecular engineer noncrystallizable copolymers which exhibit a S_A mesophase over a very large range of temperatures and provides a procedure to design a polymer exhibiting a S_A mesophase with a well-established enthalpy change associated with the S_A -isotropic phase transition.

Poly[(6-2)-co-(BVE)]X/Y

This copolymer system is different from poly[(6-11)-co-(BVE)]X/Y systems since poly(6-2) exhibits an inverse monotropic X (unidentified phase) in the first heating scan and a glassy phase in the second and subsequent heating scans.^{27b} Table II summarizes the experimental data of the copolymers, poly[(6-2)-co-(BVE)]X/Y.

The DSC traces of the first heating scans are presented in Figure 5a, those of the first cooling scans in Figure 5b, while those of the second and subsequent heating scans in Figure 5c. Data collected from second heating and first cooling scans are summarized in Table II. As determined from first heating scans, poly(6-2) with a degree of polymerization of 17 exhibits only the X phase. Upon copolymerization, the X phase shows a continuous dependence of copolymer composition over the range of compositions from $X/Y=10/0$ to $X/Y=5/5$. In addition, a nematic mesophase is induced in the copolymers with $X/Y=9/1$ to $X/Y=6/4$. This nematic phase disappears at higher dilution of the mesogenic groups (Figure 5a). This is not an unexpected result since upon copolymerization the glass transition temperature of the copolymers is lowered and therefore, copolymerization transforms the virtual nematic mesophase^{27b} into an inverse monotropic nematic one. Poly (6-2) with degrees of polymerization lower than four have a lower glass transition temperature and exhibit an enantiotropic nematic mesophase.^{27b}

In the first DSC cooling scans, both the X and the nematic mesophases do not appear (Figure 5b) since these mesophases are located in the close proximity of the glass transition temperature of these copolymers and therefore, are strongly kinetically controlled. However, upon shearing the copolymers with $X/Y=9/1$ to $X/Y=6/4$ just above their T_g on the optical polarized microscope, we can see the formation of a nematic phase. This mesophase disappears upon relaxation. The phase behavior of poly[(6-2)-co-(BVE)] X/Y determined from first heating and the cooling scans is plotted in Figure 6.

The most important conclusion obtained from the copolymerization of 6-2 with BVE is as follows. Although the mesogenic structural unit of the copolymers leads at this molecular weight to a homopolymer which exhibits either a monotropic X in the first heating scan or a glassy phase in the second heating scan, the resulting copolymers display a monotropic nematic mesophase over a quite broad range of copolymer compositions.

The results described in this paper provide one of the very few series of quantitative copolymerization experiments performed with mesogenic and non-mesogenic vinyl ethers

and confirm the previous results obtained with copolymers based on a polysiloxane backbone.¹¹ Since these pairs of monomers can be polymerized by a living mechanism, both the molecular weight and the composition of the copolymers can be conveniently controlled. These results have demonstrated how to engineer the phase transitions of a polymer exhibiting a S_A or nematic mesophase by living copolymerization of monomer pairs containing mesogenic and non-mesogenic vinyl ethers.

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FIGURE AND SCHEME CAPTIONS

Scheme I. Cationic copolymerization of 6-n with BVE

Figure 1. DSC traces displayed during the first heating scan (a), second heating scan (b), and first cooling scan (c) of poly(6-11) and of [poly(6-11)-co-(BVE)]X/Y.

Figure 2. The dependence of phase transition temperatures on the composition of [poly(6-11)-co-(BVE)]X/Y copolymers: (a) data from first heating scan: O -T_g; \diamond -T_{k-S_A}; \square -T_{S_A-i}; (b) data from second heating scan (h) and first cooling scan (c): O -T_g (h); \diamond -T_{k-S_A} (h); \square -T_{S_A-i} (h); O -T_g (c); \diamond -T_{S_A-k} (c); \square -T_{i-S_A} (c)

Figure 3. The dependence of the enthalpy change associated with the mesomorphic-isotropic and isotropic-mesomorphic phase transitions on copolymer composition for [poly(6-11)-co-(BVE)]X/Y: \square - Δ H_{S_A-i} (data from first heating scan); Δ - Δ H_{S_A-i} (data from second heating scan); O - Δ H_{i-S_A} (data from first cooling scan)

Figure 4. The dependence of the peak width ΔT (°C) of the S_A-i phase transition temperature versus the composition of [poly(6-11)-co-(BVE)]X/Y: \square -first heating scan; Δ -second heating scan; O -first cooling scan.

Figure 5. DSC traces displayed during the first heating scan (a), second heating scan (b), and first cooling scan (c) of poly(6-2) and of [poly(6-11)-co-(BVE)]X/Y.

Figure 6. The dependence of phase transition temperatures on the composition of [poly(6-11)-co-(BVE)]X/Y copolymers: (a) data from first heating (h) scan and first cooling (c) scan: O -T_g (h); \diamond -T_{X-n} (h); Δ -T_{n-i} (h); O -T_g (c).

Table I. Cationic Copolymerization of 6-11 with BVE (polymerization temperature, 0°C; polymerization solvent, methylene chloride; $[M]_0 = [6-11] + [BVE] = 0.256-0.772$ M; $[M]_0/[I]_0 = 20$; $[(CH_3)_2SiO]/[I]_0 = 10$; polymerization time, 1 hr) and Characterization of the Resulting Copolymers. Data on first line are from first heating and cooling scans. Data on second line are from second heating scan.

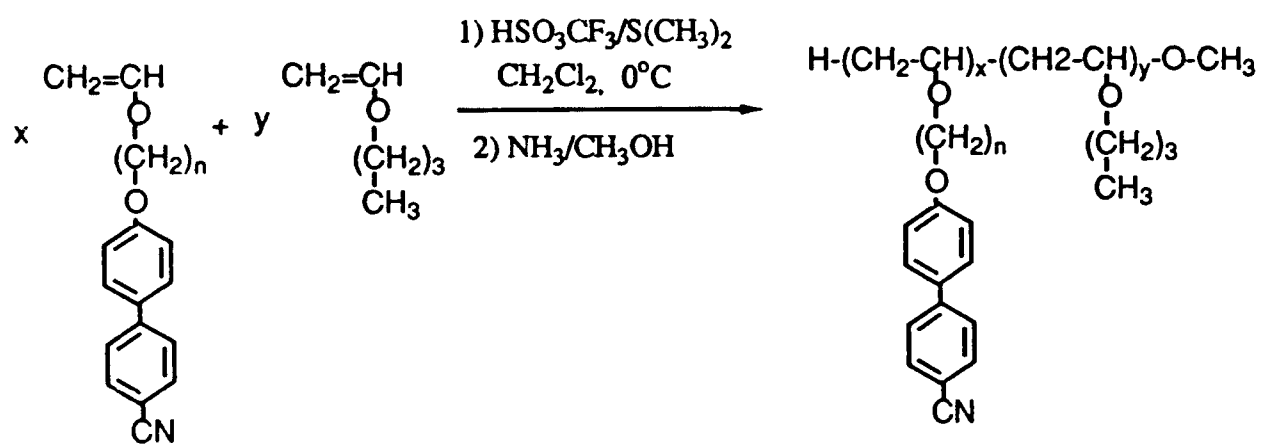
Sample No.	[6-11]/[BVE] (mol/mol)	Polymer yield(%)	Mn $\times 10^{-3}$	Mw/Mn	D P	phase transitions (°C) and corresponding enthalpy changes (kcal/mru)	
						heating	cooling
1	1/9	58	2.8	1.12	22	g -26.1 i g -27.8 i	i -35.2 g
2	2/8	69	3.5	1.09	22	g -15.7 S _A 30.3 (0.09) i g -16.5 S _A 30.8 (0.07) i	i 29.2 (0.08) S _A -18.2 g
3	3/7	84	3.8	1.14	20	g -10.6 S _A 49.3 (0.21) i g -11.4 S _A 48.9 (0.18) i	i 48.0 (0.16) S _A -18.2 g
4	4/6	75	4.1	1.12	20	g -5.3 S _A 66.6 (0.31) i g -5.5 S _A 65.2 (0.23) i	i 61.7 (0.22) S _A -12.9 g
5	5/5	78	4.5	1.07	18	g -0.5 S _A 89.7 (0.37) i g -0.25 S _A 89.2 (0.41) i	i 83.2 (0.35) S _A -10 g
6	6/4	79	4.6	1.13	17	g 3.7 S _A 105.9 (0.51) i g 2.5 S _A 105.6 (0.44) i	i 100.5 (0.45) S _A -6.1 g
7	7/3	85	5.3	1.08	17	g 7.1 k 53.2 (0.28) S _A 122.0 (0.58) i g 5.7 S _A 122.0 (0.52) i	i 112.4 (0.56) S _A -1.1 g
8	8/2	80	5.9	1.15	17	g 10.9 k 55.1 (2.27) S _A 137.4 (0.65) i g 9.5 S _A 137.2 (0.69) i	i 129.0 (0.68) S _A 1.4 g

9	9/1	87	6.1	1.12	17	g 12.1 k 57.8 (2.66) sA 148.6 (0.75) i g 12.1 sA 148.6 (0.79) i	i 140.8 (0.76) sA 2.9 g
10	10/0	81	8.2	1.12	19	g 14.5 k 57.1 (3.45) sA 157.2 (0.90) i g 14.0 sX 44.2 (0.93) sA 156.4 (0.87) i	i 149.4 (0.89) sA 18.9 (0.63) sX 8.8 g

Table II. Cationic Copolymerization of 6-2 with BVE (polymerization temperature, 0°C; polymerization solvent, methylene chloride; $[M]_0=[6-2]+[BVE]=0.256-0.680$ M; $[M]_0/[I]_0=20$; $[(CH_3)_2S]_0/[I]_0=10$; polymerization time, 1hr) and Characterization of the Resulting Copolymers. Data on first line are from first heating and cooling scans. Data on second line are from second heating scan.

Sample No.	[6-2]/[BVE] (mol/mol)	Polymer yield(%)	Mnx 10 ⁻³	Mw/Mn	D P	phase transitions (°C) and corresponding enthalpy changes (kcal/mru)	
						heating	cooling
1	3/7	65	2.6	1.10	18	g 8.1 i g 7.2 i	i -4.5 g
2	4/6	63	2.5	1.10	16	g 12.0 i g -12.0 i	i 3.3 g
3	5/5	72	3.2	1.14	18	g 22.1 X 22.9 (0.05) i g 22.0 i	i 12.3 g
4	6/4	75	3.2	1.09	17	g 30.0 X 38.2 (0.10) n 59.2 (0.02) i g 28.4 i	i 19.5 g
5	7/3	70	3.7	1.12	18	g 39.2 X 46.7 (0.20) n 66.7 (0.03) i g 41.0 i	i 29.4 g
6	8/2	70	3.8	1.08	17	g 55.1 X 64.7 (0.35) n 79.6 (0.06) i g 53.8 i	i 45.4 g

7	9/1	76	4.1	1.14	17	g 67.1 X 72.9 (0.36) n 84.2 (0.05) i	i 57.5 g
8	10/0	65	4.6	1.18	17	g 81.0 X 85.7 (0.25) i	i 70.5 g



Scheme I

Poly[(6-11)-co-(BVE)]X/Y

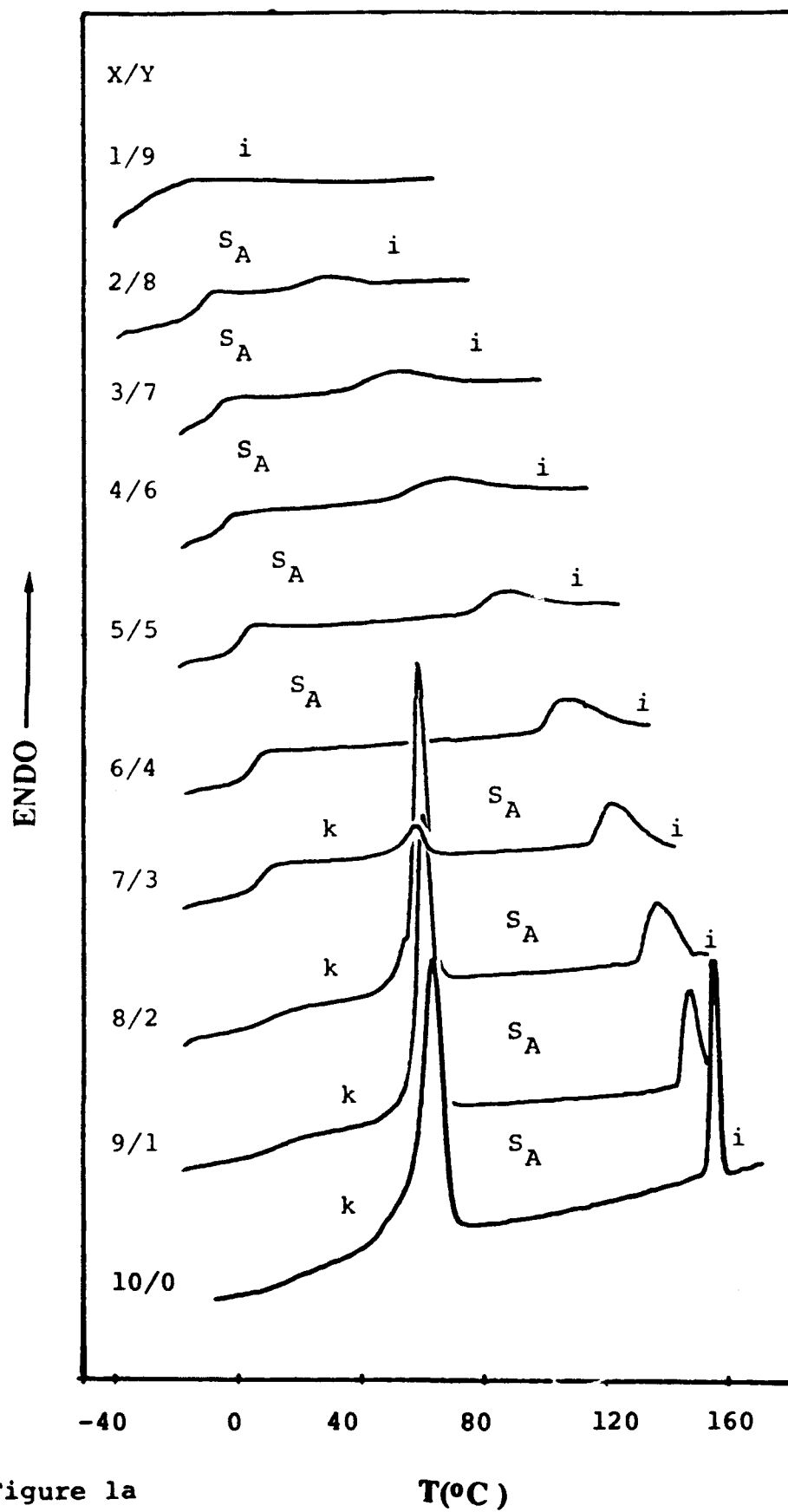


Figure 1a

T(°C)

Poly[(6-11)-co-(BVE)]X/Y

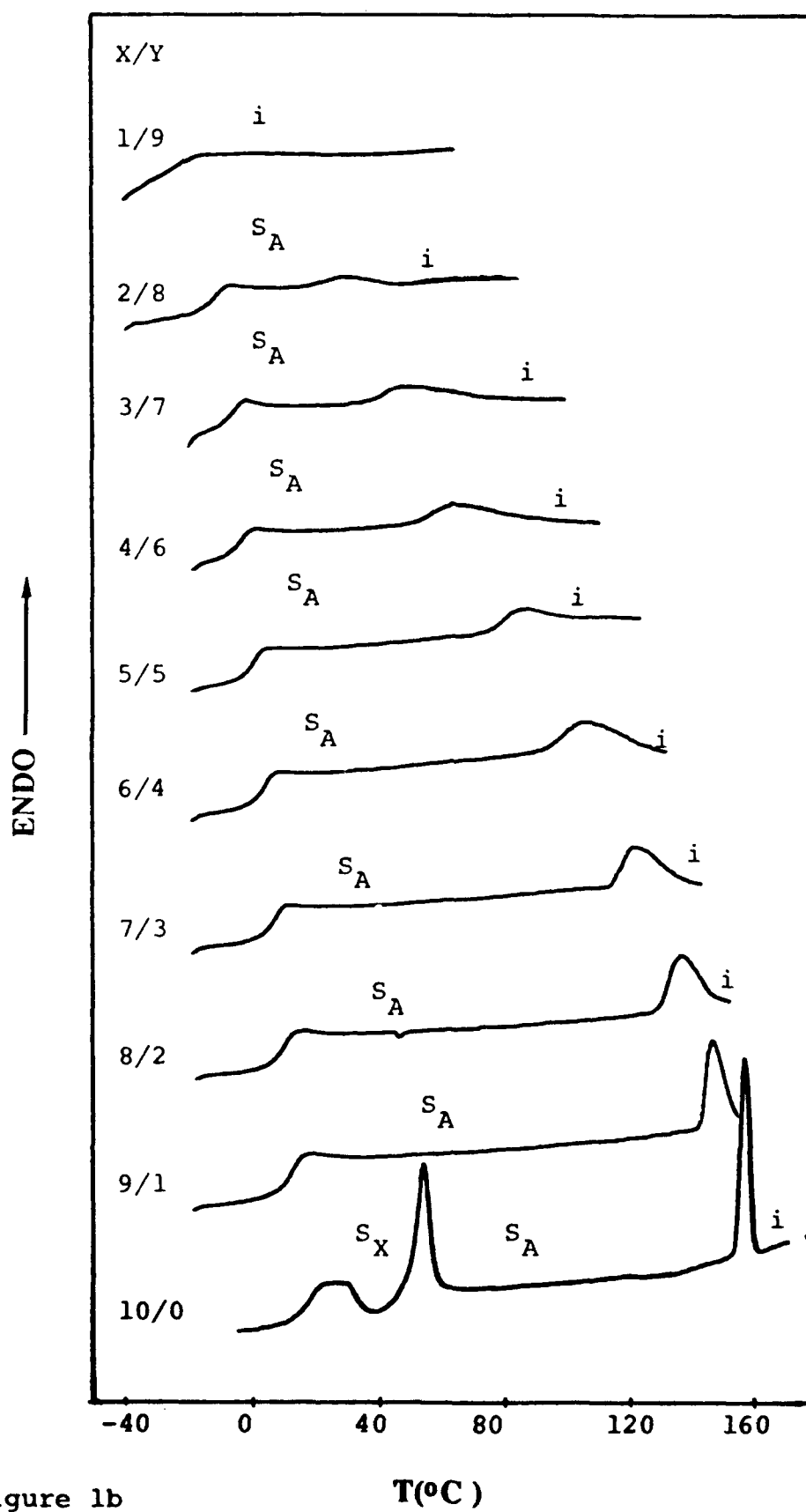


Figure 1b

Poly[(6-11)-co-(BVE)]X/Y

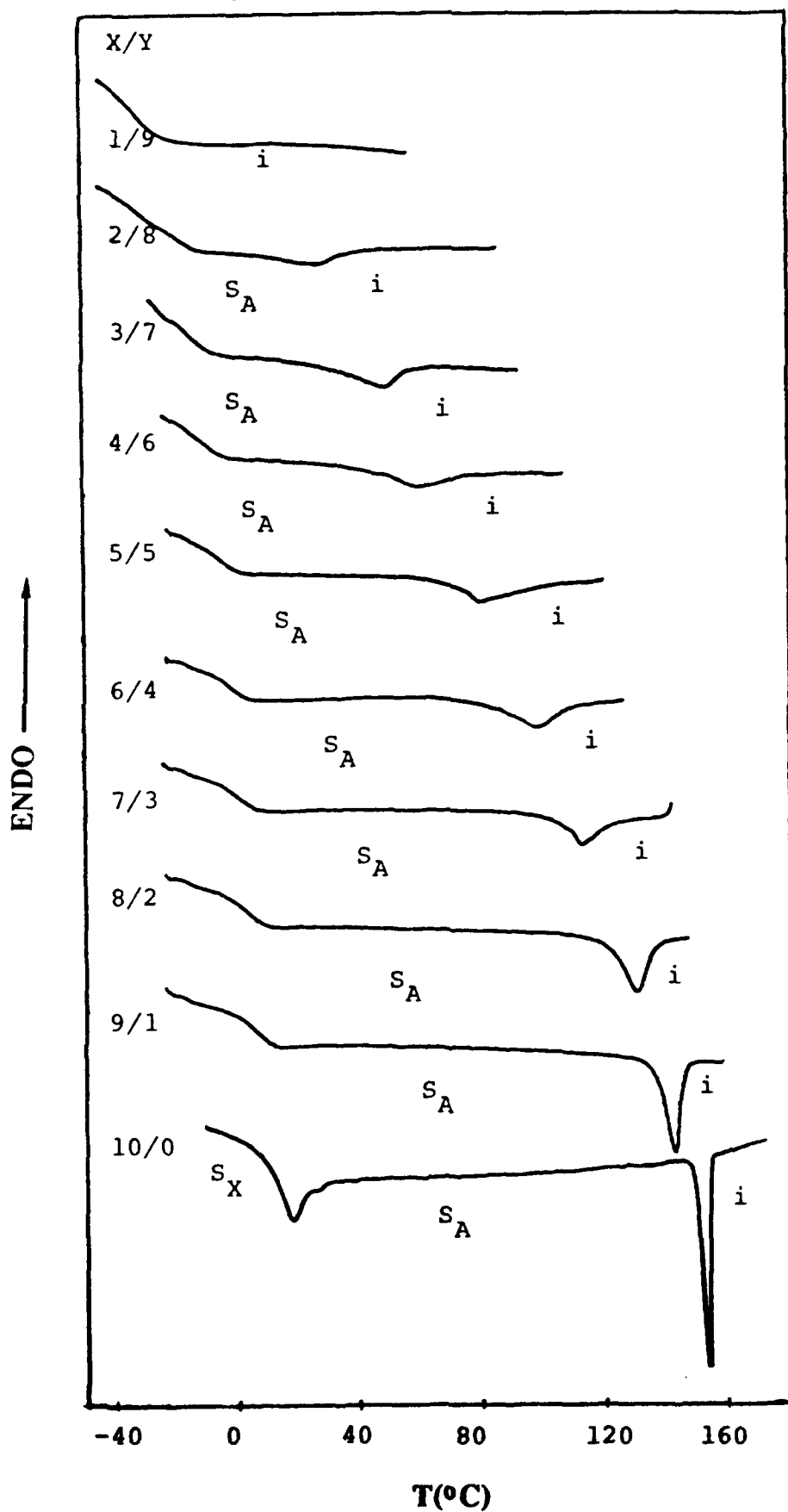


Figure 1c

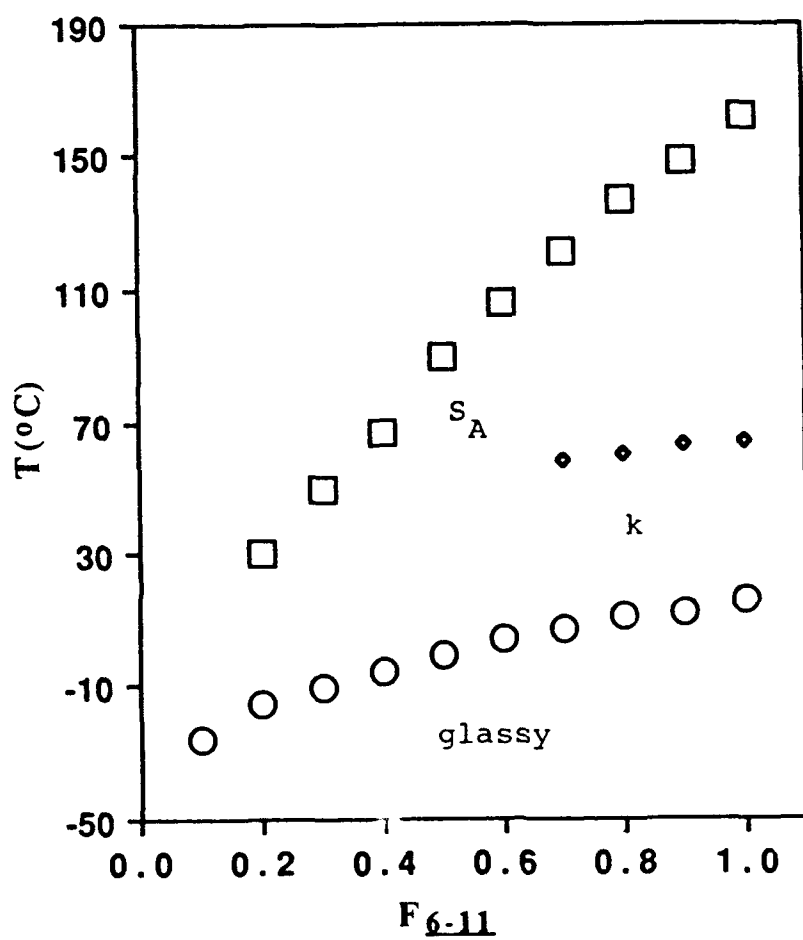


Figure 2a

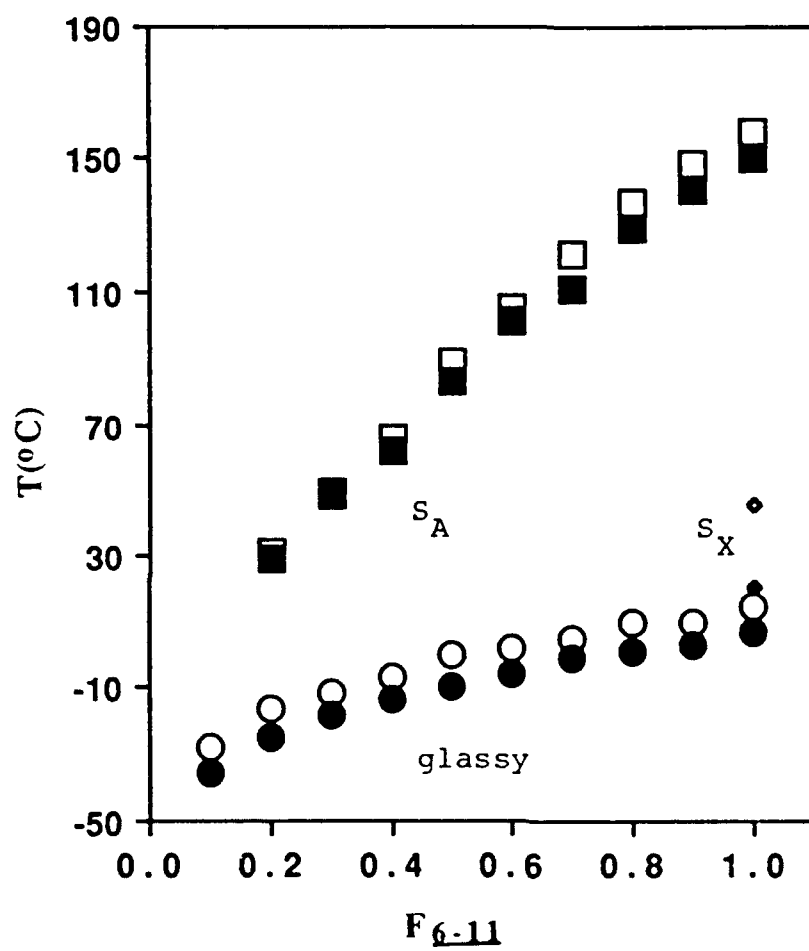


Figure 2b

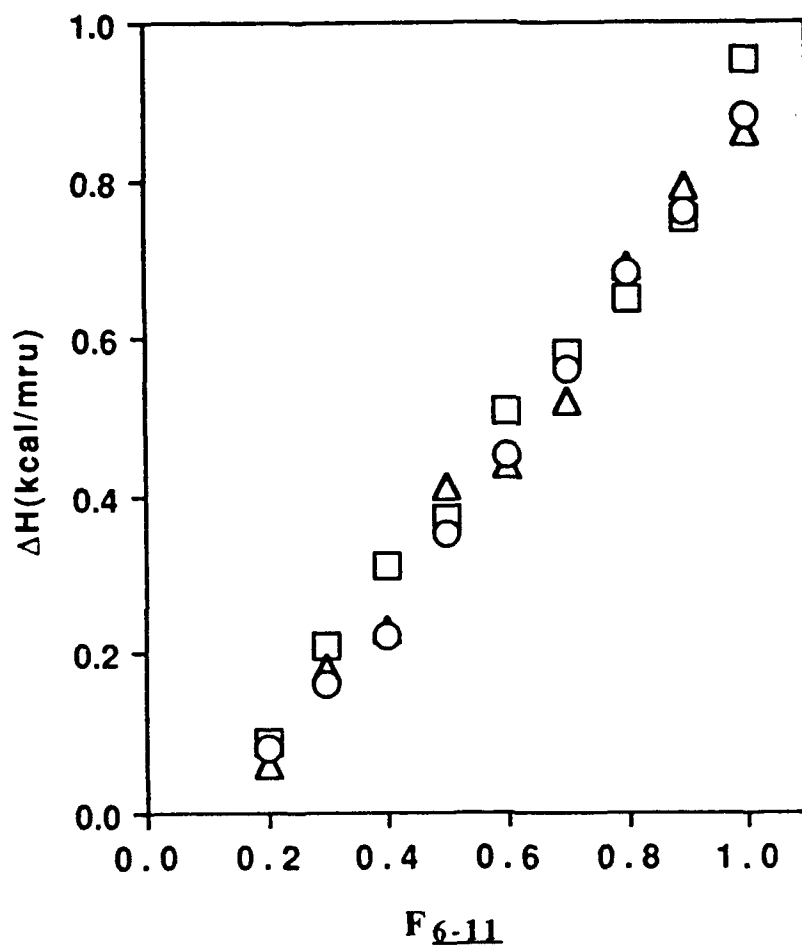


Figure 3

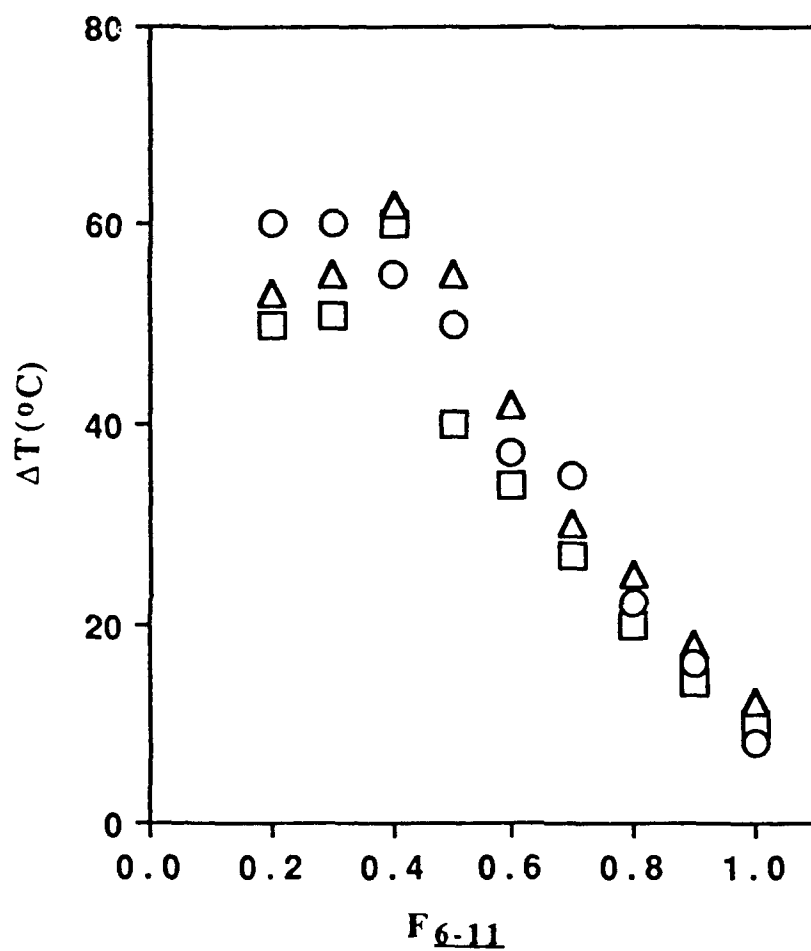


Figure 4

Poly[(6-2)-co-(BVE)]X/Y

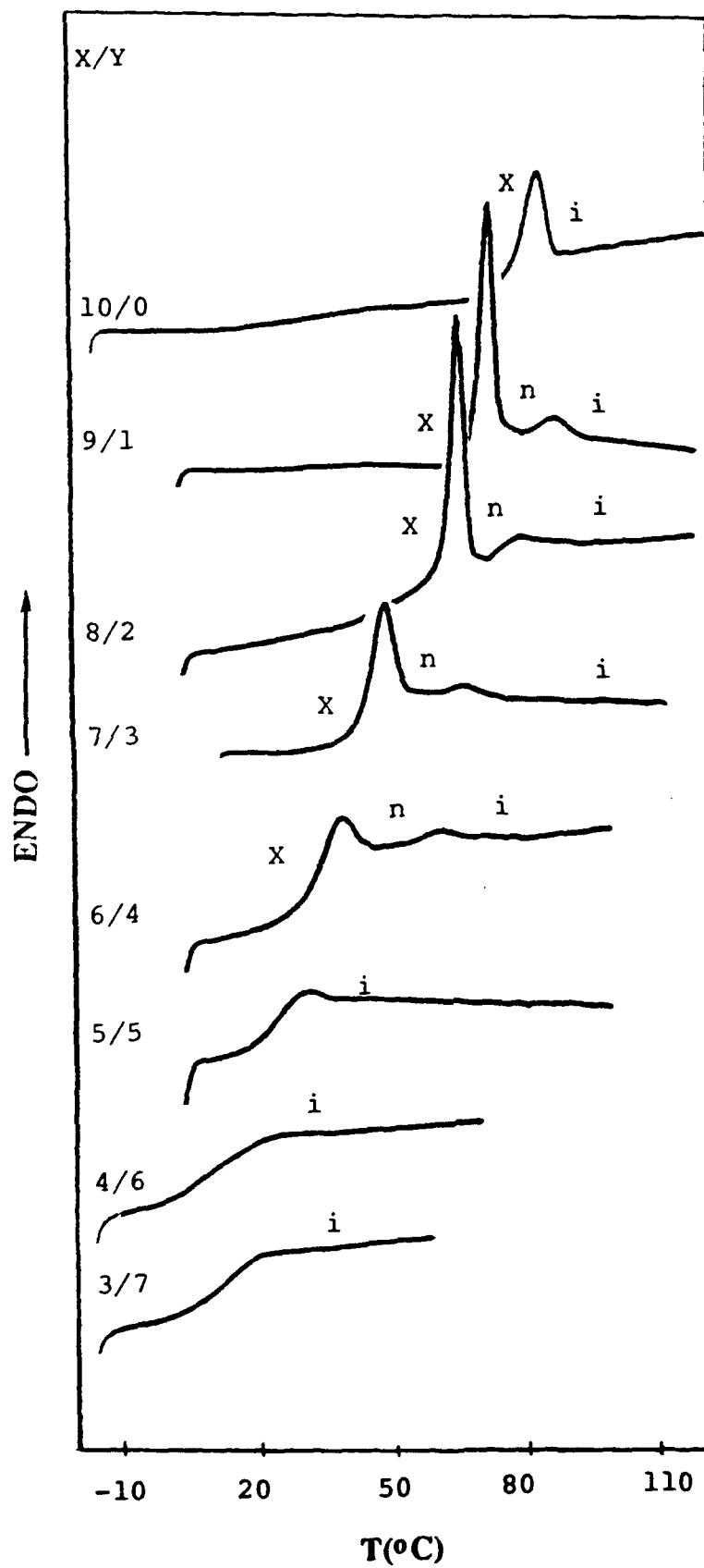


Figure 5a

Poly[(6-2)-co-BVE]X/Y

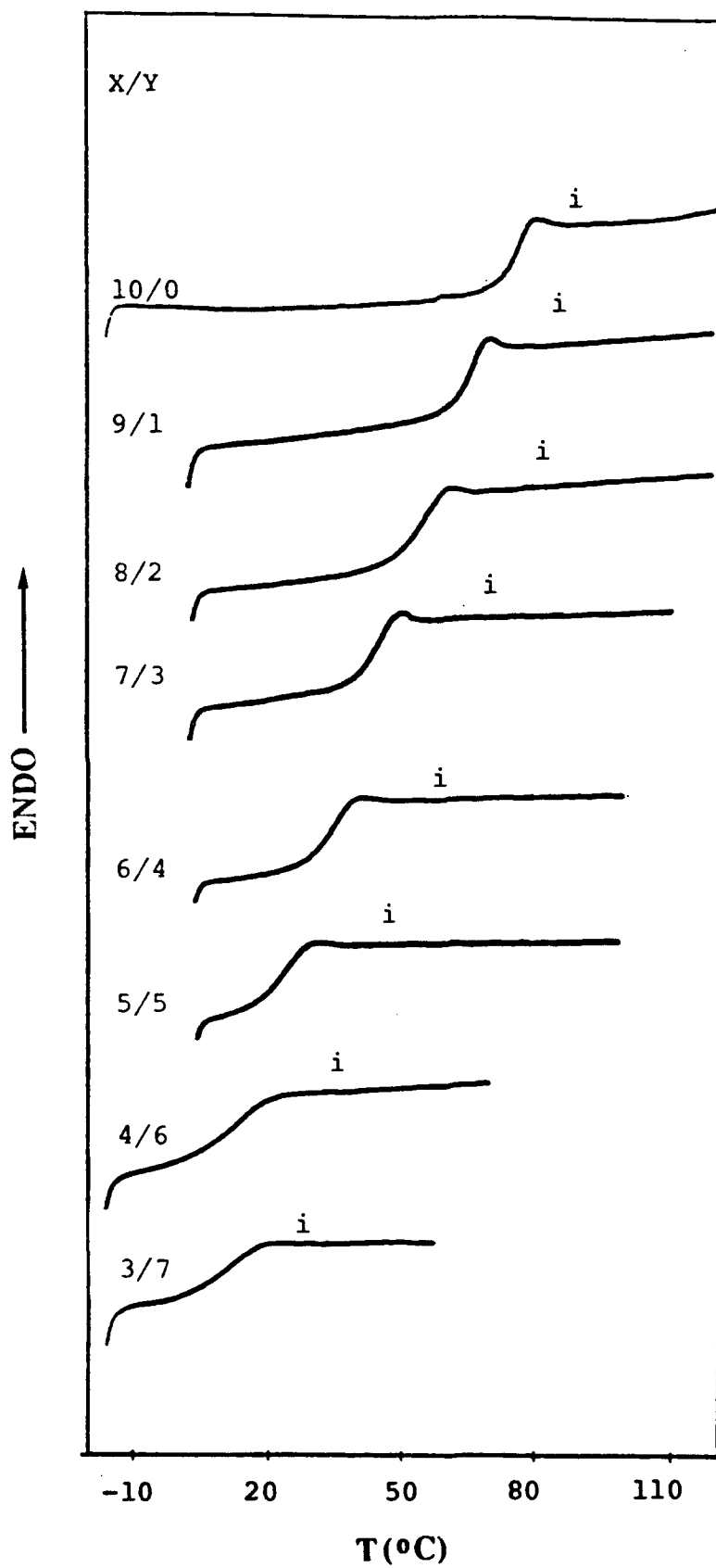


Figure 5b

Poly[(6-2)-co-(BVE)]X/Y

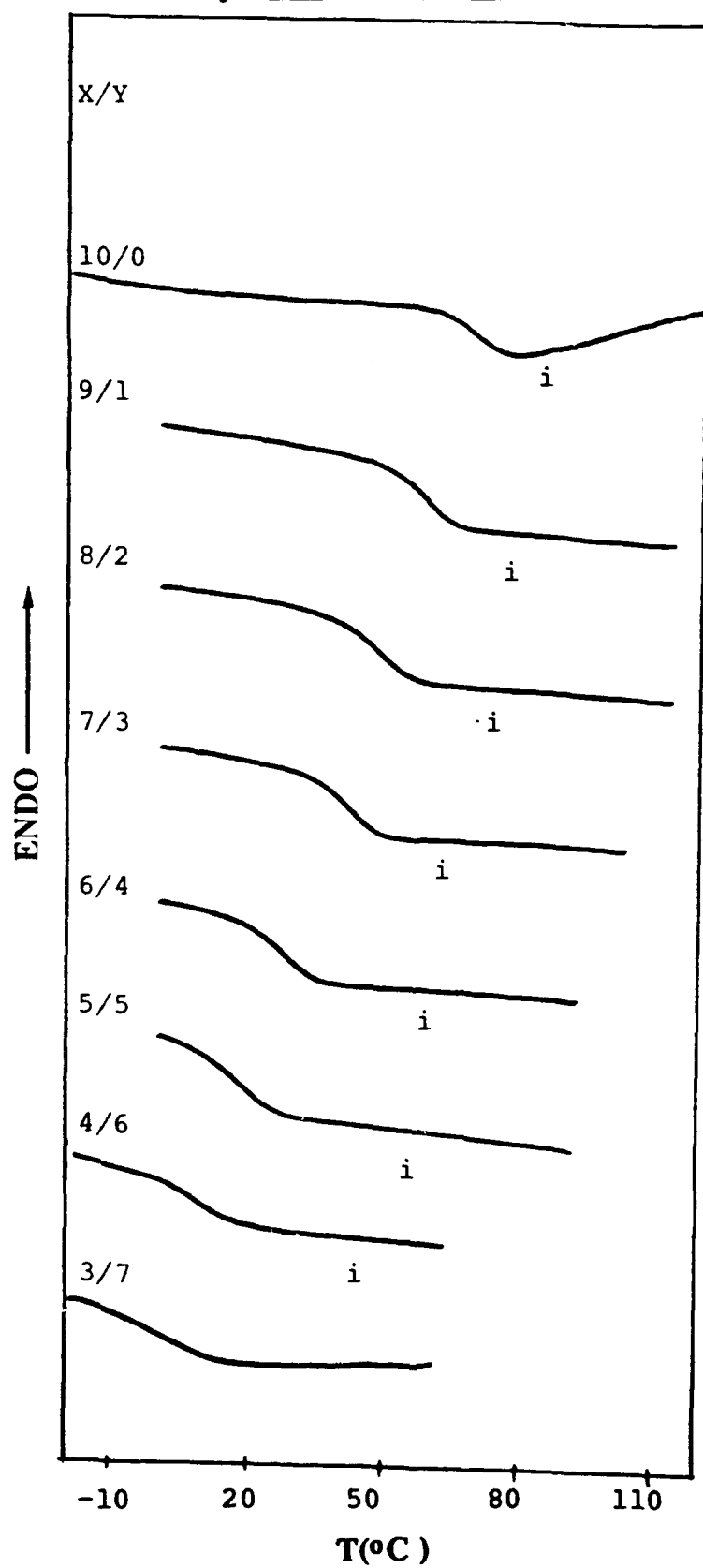


Figure 5c

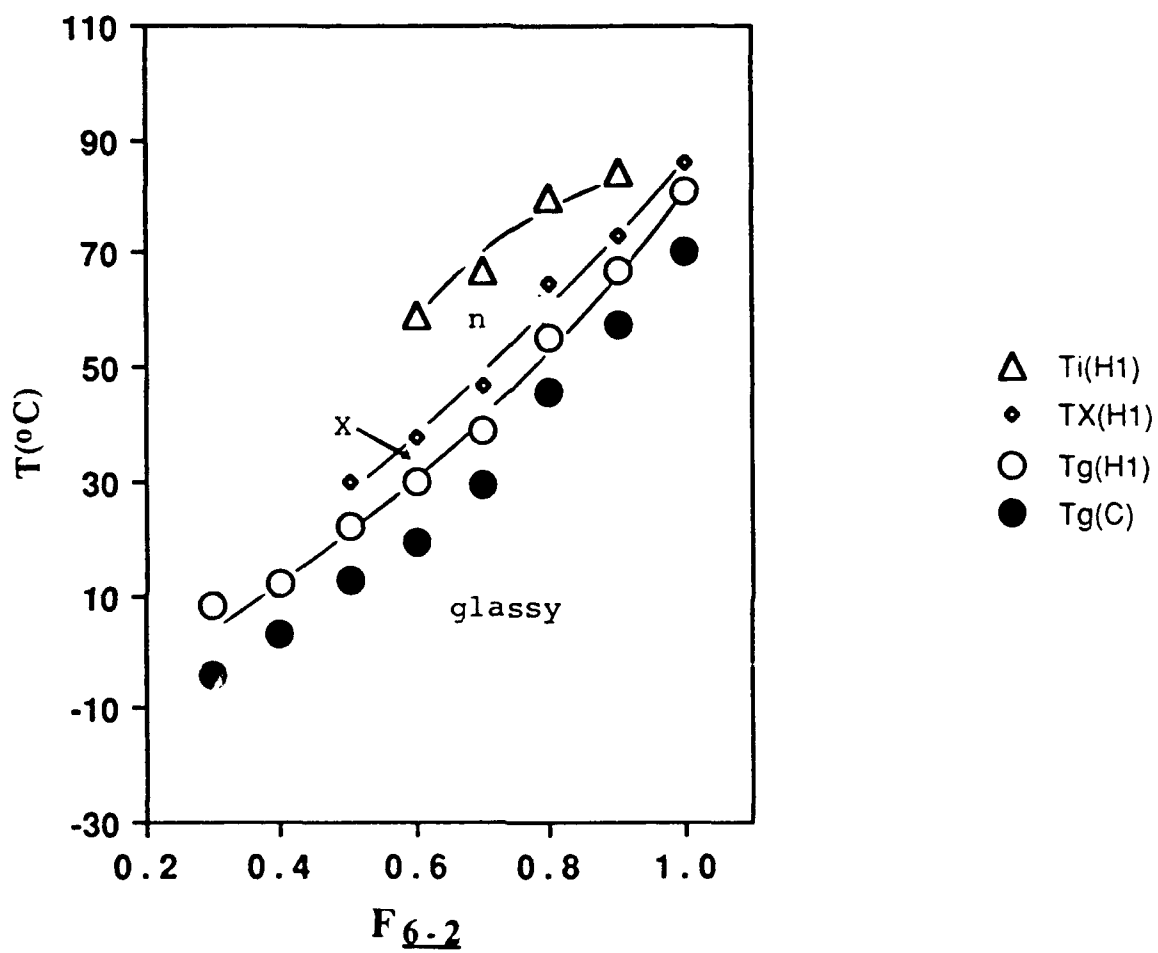


Figure 6